MICRO-DETERMINATION OF CERIUM

By I. PÉNZES and L. J. CSÁNYI

Institute of Inorganic and Analytical Chemistry, Attila József University, Szeged

Copper(II) phtalocyanine, methylene blue and iron(II) have been recommended for the micro-determination of cerium(IV) in the presence of cerium(III). — Optical interaction between cerium(IV) and cerium(III) has been observed when cerium(IV) is present in form of hydroxo complexes.

There are many useful volumetric macro methods for the determination of cerium(IV) ions, but these are not precise enough on micro scale [1]. For this reason it was necessary to find better ways for the estimation of cerium(IV) in minute quantities.

1. Determination of cerium (IV) based on its own colour

It is well known that cerium(IV) ions strongly absorb the light at 320 nm, in 0,4 M sulphuric acid, $\varepsilon = 5540$ l. mole^{-1} cm^{-1}. This behaviour makes possible the spectrophotometric determination of cerium(IV) [2]. The estimation based on the absorbance, however, can be carried out only under strictly defined experimental conditions. Namely, cerium(IV) ions hydrolize even at low pH values, cerium(IV) hydroxide or basic salts being precipitated. This can be avoided by adjusting the sulphuric acid concentration at least to 0.4 M.

When cerium(IV) ions are present in form of hydroxo complexes and the solution contains cerium(III) ions as well, an optical interaction can be observed. From this follows that the amount of cerium(IV) ions determined spectrophotometrically depends on the concentration of cerium(III) present. The extent of the optical interaction is the greatest in presence of perchloric acid, while somewhat smaller in nitric acid and the smallest in a sulphuric acid medium.

Reliable analytical data for cerium(IV) ions can be obtained only in absence of cerium(III). The measurement can then be carried out in the following way: The acid concentration is adjusted to 0.4 M by sulphuric acid and the absorbance measured at 320 nm. The Lambert—Beer law holds in the range of $10^{-6} - 10^{-4}$ M and the concentration of cerium(IV) can be calculated by using the value of the extinction coefficient given above.

2. *Determination of cerium (IV) by oxidation of different dyestuffs*

When the solution to be analysed contains cerium(III) ions, too, other ways are to be looked for to determine the cerium(IV) ions. To this end a series of dyestuffs was tested. The following were found suitable for the determination based on the bleaching effect of cerium(IV).

a) *Determination with the aid of copper (II) phtalocyanine complex*

The copper(II) complex of phtalocyanine is readily soluble in water, the obtained blue solution absorbs the light at 620 nm, and its extinction coefficient is as high as 42 000 l. mole^{-1} cm^{-1}. The complex reacts with cerium(IV) ions rapidly. On adding the oxidizing agent to the dye solution, transitorily a red colour is developed, the disappearence of which takes a longer time especially when the concentration of cerium(IV) is relatively high. This phenomenon may be ascribed either to a multistep oxidation process or to the disproportionation reaction of the red intermediate. For the analysis the following procedure may be suggested:

Adjust the acid concentration of the solution to be analysed to 0.4 M by sulphuric acid and add the aqueous solution of the copper(II) phtalocyanine reagent drop by drop in a quantity to obtain a dye concentration of about 2.10^{-5} M. After having filled the graduated flask, measure the absorbance at 620 nm. If proceeding so, the dyestuff will be rapidly oxidized on the effect of cerium(IV) to the final state and thus the measurement can be carried out immediately. By this method 0,03—0,3 μM cerium(IV) can be determined with $\pm 3\%$ relative error. Cerium(III) ions present do not interfere with the analysis, while strong oxidizing reagents do.

The aqueous solution of the reagent can be stored without any decomposition for a longer time. — It is necessary to call attention to the fact that the absorbance of the dye markedly depends on temperature.

b) *Determination of cerium (IV) by methylene blue*

The reaction between methylene blue and cerium(IV) ions may also be applied to analytical purposes [3]. In 1 M sulphuric acid methylene blue has a high absorption peak at 755 nm (the extinction coefficient is 52 600 l. mole^{-1} cm^{-1}) and the Lambert—Beer law holds. Under such experimental conditions the dye instantaneously reacts with cerium(IV) ions, 1 mole methylene blue and cca. 4.5 mole cerium(IV) being involved in the reaction.

In neutral solutions, however, depending on the dye concentration, rather involved association equilibria exist, which result in a great change in the absorbance of the dye.

According to our experiences reliable data can be obtained by the following procedure:

The sample to be analysed is pipetted into a graduated flask of 25 ml containing 3—4 ml of 10^{-4} M methylene blue solution and sulphuric acid sufficient, taking into account also the acid content of the sample, to attain 1 M total acid concentration at the end volume. The flask is then shaken thoroughly and filled up to the mark. The absorbance of the solution is measured at 755 nm by using 1 M

sulphuric acid as blank. The drop in the absorbance caused by cerium(IV) is proportional to its concentration. By this method $0,1—1,0\ \mu M$ of cerium(IV) can be estimated with $\pm 1,5\%$ relative error.

c) *Determination of cerium(IV) by iron(II) ions*

The interference of cerium(III) can also be avoided by reducing cerium(IV) ions with iron(II) and measuring the light absorption of the iron(III) formed. At about 0.8 M acid concentration the reaction is instantaneous. For determination the following procedure may be suggested. Pour the sample in a graduated flask of 25 ml containing 10 ml of 10^{-2} M $FeSO_4$ and sulphuric acid in a quantity to get 0.4 M acid concentration at the end volume. The flask is filled up to the mark, then the absorption of iron(III) is measured at 304 nm. The estimation of $1.2—12.5\ \mu M$ cerium(IV) can be carried out with $\pm 2\%$ relative error. It should be mentioned that cerium(III) ions also absorb the light at 304 nm, the extinction coefficient is, however, only 26 l mole^{-1} cm^{-1}. Consequently, cerium(III) does not interfere heavily when its concentration is commensurable with that of cerium(IV).

Ferroin was also applied to the determination of cerium(IV) but, contrary to literature, [4] no reliable results were obtained.

References

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МИКРО-ОПРЕДЕЛЕНИЕ ЦЕРИЯ(IV)

И. Пензеш и Л. Й. Чани

Для определения микро-количеств церия(IV) в присутствии церия(III) авторами рекомендовались фталоцианин меди(II), метиловый голубой и железо(II). Если церий(IV) имеется в виде гидроксо комплексов, оптическое взаимодействие между цериями (IV) и (III) было наблюдено.